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Abstract
The concentration of uranium in soil has been determined for 80 sites in an area suspected to have uranium contamination by in situ laser ablation- inductively coupled plasma atomic emission spectrometry (LA-ICPAES), utilizing a field-deployable mobile analytical laboratory. For 15 of the 80 sites analyzed, soil samples were collected so that the field LA-ICPAES results could be compared to laboratory-determined values. Uranium concentrations determined in the field by LA-ICPAES for these 15 sites range from <20 parts per million>(ppm) by weight to 285 ppm. The uncertainty in the values determined, however, is large relative to the uranium concentrations encountered at this site. The 95% confidence interval (CI) values are approximately 85 ppm. The uranium concentrations determined by laboratory LA- ICPAES analysis range from <20 to 102 ppm>(95% CI of approximately 50 ppm); microwave dissolution and subsequent standard addition determination of uranium by solution nebulization ICPAES using an ultrasonic nebulizer yields 19-124 ppm uranium (95% CI of approximately 10 ppm). For 11 of the 15 samples, the field- and laboratory-determined uranium concentrations agree, within the uncertainty of the determined values.

Keywords
uranium, analytic method, atomic emission spectrometry, concentration, diagnostic value, laser, quality control, radiation exposure, soil pollution

Comments
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In Situ Determination of Uranium in Soil by Laser Ablation-Inductively Coupled Plasma Atomic Emission Spectrometry

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The concentration of uranium in soil has been determined for 80 sites in an area suspected to have uranium contamination by in situ laser ablation-inductively coupled plasma atomic emission spectrometry (LA-ICPAES), utilizing a field-deployable mobile analytical laboratory. For 15 of the 80 sites analyzed, soil samples were collected so that the field LA-ICPAES results could be compared to laboratory-determined values. Uranium concentrations determined in the field by LA-ICPAES for these 15 sites range from <20 parts per million (ppm) by weight to 285 ppm. The uncertainty in the values determined, however, is large relative to the uranium concentrations encountered at this site. The 95% confidence interval (CI) values are approximately 85 ppm. The uranium concentrations determined by laboratory LA-ICPAES analysis range from <20 to 102 ppm (95% CI of approximately 50 ppm); microwave dissolution and subsequent standard addition determination of uranium by solution nebulization ICPAES using an ultrasonic nebulizer yields 19–124 ppm uranium (95% CI of approximately 10 ppm). For 11 of the 15 samples, the field- and laboratory-determined uranium concentrations agree, within the uncertainty of the determined values.

Introduction

Laser ablation is a technique that enables sampling and analysis to be performed for solid samples without acid dissolution of the samples. Laser radiation, focused onto the surface of the sample, causes vaporization and ejection of material from the surface (*1–3*). Analytical techniques that utilize the optical emission from the primary laser plasma generated by the interaction of the laser with the sample have been developed (*4*). More frequently, the laser ablated vapor and particulates are transported to a secondary plasma source such as the DC argon plasma (*5*), microwave-induced plasma (*6*), or inductively coupled plasma (*1,2,7–11*) for subsequent atomization, ionization, and excitation of the ablated material. Laser ablation-inductively coupled plasma analyses have been performed using both atomic emission spectrometry (ICPAES) and mass spectrometry (ICPMS) for detection of laser ablated samples. Since there is virtually no limitation on the type of solid that can be subjected to laser ablation, a wide variety of samples have been analyzed, including metals, ceramics, and geological samples such as rocks, soils, and sediments.

Characterization of soils and inorganic hazardous wastes at U.S. Department of Energy (DOE) and Environmental Protection Agency (EPA) remediation sites and other contaminated sites is one potentially important application for laser ablation sampling. Utilization of a mobile analytical laboratory in conjunction with laser ablation techniques may provide an advantageous alternative to conventional sampling methodologies. Sampling and analysis can be performed "in field", eliminating sample collection, transport, storage, and disposal. Minimizing the number of steps in the handling process minimizes potential contamination or alteration of the sample and potential exposure of workers to hazardous materials. Since little or no sample preparation is required for laser ablation, analyses can be performed rapidly, with high throughput and minimal turn-around time. In addition, soils can be analyzed prior to and following any site remediation to determine if the remediation actions performed are adequate.

This paper presents the results obtained for characterization of a site suspected to have uranium contamination. Uranium concentrations were determined by remote laser ablation-inductively coupled plasma atomic emission spectrometry (LA-ICPAES) utilizing a field-deployable mobile analytical laboratory. This was the initial testing and operation of the mobile lab in a field setting. For 15 of the 80 sites analyzed by LA-ICPAES in the field, soil samples were collected for laboratory analysis and comparison with the field-determined uranium concentrations. Two methods of analysis were performed in the laboratory, LA-ICPAES and microwave dissolution with standard addition determination of uranium by solution nebulization ICPAES.

Experimental Section

Field LA-ICPAES System. The mobile laboratory houses all the equipment required to analyze soil samples for various inorganic contaminants (chromium, lead, thorium, uranium) using the LA-ICPAES technique. The design and operational characteristics of the mobile laboratory have been described (*12*). The mobile lab consists of an 11-m-long fifth-wheel trailer, a medium-duty truck, and an instrumentation platform that is connected to the rear of the trailer. A diesel generator provides electrical power for the LA-ICPAES instrumentation and for utilities such as lighting and air conditioning. Water and gases (argon and nitrogen) required by the equipment are also available. The majority of the instrumentation is housed in the trailer. This includes a Continuum NY81-20 Nd:YAG laser, a Thermo Jarrell Ash (TJA) ICAP 61E spectrometer, an RF Plasma Products ICP-16L generator, a NesLab Model HX-150 water recirculator, computers, video monitors, and other electronic equipment. The instrumentation platform houses an ICP torchbox, a standards sampling station, and a robotic arm that can be used to place an end effector at the soil site to be sampled. The end effector can also be removed from the robotic arm and manually positioned at the site to be analyzed.

Frequency-doubled laser radiation from the Nd:YAG laser (320 mJ/pulse, 532 nm, 20 Hz, 7 ns pulsewidth) is attenuated using two beamsplitters and a variable aperture. The attenuated laser beam is coupled into a 25-m-

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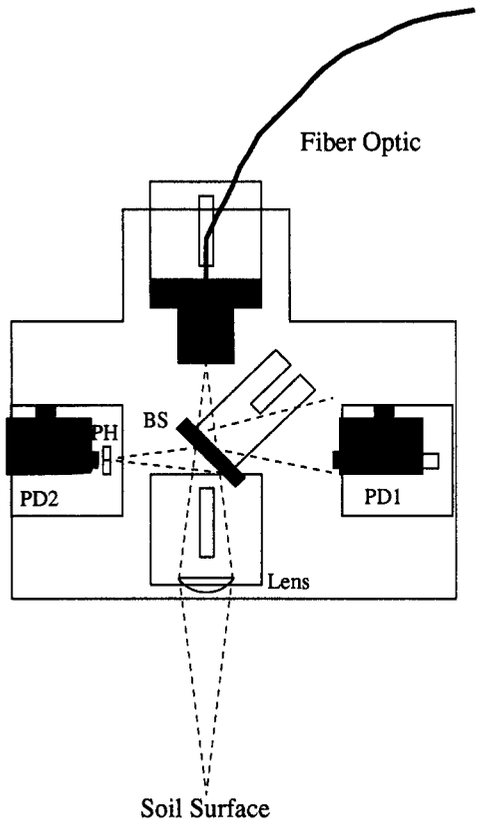

Figure 1. Optical components in the end effector of the mobile laboratory LA-ICPAES system. A quartz beamsplitter (BS) diverts a portion of the diverging fiber optic output to a photodiode (PD1) so that the fiber-delivered laser power can be monitored. A 25-mm diameter, 50-mm focal length lens is used to focus the laser radiation onto the surface of the soil. Light reflected from the soil surface is collected by the lens, reflects off the BS, and passes through a 600-μm aperture pinhole (PH) to the photodiode (PD2). The focus is optimized by adjusting the position of the optical components relative to the soil surface to maximize the voltage at PD2.

long, 600-μm core diameter silica core, silica clad, fiber optic cable that is routed out of the mobile lab to the soil site to be analyzed. A 25-mm diameter, 50-mm focal length lens is used to focus the attenuated laser beam. The face of the fiber optic cable is positioned slightly beyond the focal point of the lens, so that the diverging beam fills approximately 85% of the fiber core diameter. Positioning the fiber in the diverging beam overcomes self-focusing in the fiber and subsequent damage in the first few centimeters of the fiber (*13*, *14*). Typical laser pulse energies incident on the face of the fiber are 5 mJ, with fiber optic output energies of 3 mJ. The end effector is positioned at the site to be sampled; the ablation cell (at the bottom of the end effector) has a circular knife edge that penetrates into the soil. Water is applied to the soil surface to form a gas-tight seal so that the ablated soil sample can be transported to the ICP. The optical components in the end effector are shown in Figure 1. All of the optical components, including the output of the fiber optic cable, are mounted on an *XYZ* stage. A portion of the diverging fiber optic output is directed to a photodiode (PD1) using a quartz beamsplitter (BS) so that the fiber-transmitted laser power can be monitored. A 25-mm diameter, 50-mm focal length lens is used to focus the fiber optic-delivered laser radiation onto the surface of the soil sample to be analyzed, at the bottom of the ablation cell. The focus is monitored by imaging the focused laser spot onto PD2. Light reflected from the surface of the soil is collected by the lens, and the back surface reflection from the beamsplitter is imaged through a 600-μm aperture pinhole to PD2. The focus is optimized by adjusting the *Z*-axis position relative to the soil surface to maximize the voltage at PD2. Once the focus is optimized, the *X*- and *Y*-axes are used to raster the focused laser beam in a spiral pattern over an area of approximately 1 in. squared. The material ablated from the surface of the soil is swept out of the ablation cell by argon gas flowing at a rate of 1 L/min, through a 15-m length of 3/16-in. i.d. polyvinyl tubing, and into the ICP torch mounted on the instrumentation platform. Due to imperfect seals between the ablation cell and the soil surface, argon gas flows as high as 2 L/min are required on the ablation cell input to maintain a 1 L/min return flow to the ICP torch. A 25-mm diameter, 25-mm focal length lens is used to collect the ICP emission (f/2 collection) and focus it onto the face of a 12-m-long fiber bundle that is routed back to the TJA spectrometer in the mobile lab. The fiber bundle consists of 61 fibers of 100-μm diameter in a round-to-round arrangement (1.12-mm diameter input and output). The output end of the fiber bundle is coupled to the f/20 transfer optics of the TJA spectrometer using a 38-mm diameter, 75-mm focal length lens, with a resulting magnification of the fiber bundle output of approximately 10 at the entrance slit of the spectrometer. The TJA spectrometer is a 20-channel simultaneous spectrometer that is used to detect ICPAES signals for 19 elements. Two of the channels are used to detect uranium (U) emission signals. Channels for soil matrix elements such as silicon (Si), aluminum (Al), and iron (Fe) are also present. The experimental conditions used for the field LA-ICPAES analysis are summarized in Table 1.

The mobile lab is designed so that an operator can, in principle, direct the entire sampling and data acquisition process from inside the mobile lab by computer control of the instrumentation. The ablated sample material is confined to the ablation cell, transfer tubing, ICP torchbox, and a high-efficiency particulate air filter on the instrumentation platform. This arrangement minimizes exposure of the operator to potentially hazardous samples.

Laboratory Analysis. Soil samples from 15 of the 80 sites analyzed in the field by LA-ICPAES were collected for laboratory analysis. Roughly 35 g of topsoil was removed from each sample site. Sample preparation involved removing organic debris manually, drying the sample overnight, and subsequently pulverizing the soil sample using a ball mill. The 15 samples were analyzed by LA-ICPAES in the laboratory and by microwave dissolution with standard addition determination of U using solution nebulization ICPAES.

The laser used for the laboratory LA-ICPAES determinations is a frequency-doubled, 10-Hz repetition rate, Quantel YG481 Nd:YAG laser. Laser radiation is coupled into a 20-m-long, 600-μm core diameter fiber optic cable in a manner similar to that described for the mobile laboratory system. The output from the fiber optic is focused onto the surface of the soil sample, which is contained in an aluminum sample cup in the bottom of a glass ablation cell. A short length of tygon tubing (3 m of 3/16-in. i.d. tubing) connects the ablation cell to the ICP torch. Argon gas flowing through the ablation cell transports the laser-ablated soil material from the ablation cell to the ICP torch. The ICP system is an RF Plasma

Table 1. Experimental Conditions for Field LA-ICPAES

Fiber Optic-Delivered Laser Radiation	
laser	Continuum NY81-20 Nd:YAG
wavelength (nm)	532
repetition rate (Hz)	20
pulse duration (ns)	7
fiber optic cable length (m)	25
fiber optic cable core diameter (μm)	600
Ablation Conditions	
fiber optic output energy at sample (mJ)	3
average output power (mW)	60
peak power density at sample (MW/cm²)	100
laser spot diameter at sample (μm)	600
transport tubing	15-m length, 3/16-in. i.d.
Inductively Coupled Plasma	
ICP system	RF Plasma Products ICP-16L
RF frequency (MHz)	40
RF power (kW)	1.1
plasma gas flow rate (L/min)	16
auxiliary gas flow rate (L/min)	0.8
sample gas flow rate (L/min)	1.0
imaging	emission coupled to ICAP 61E via a 12-m-long fiber optic bundle

Spectrometer and Detection System: Thermo Jarrell Ash Model ICAP 61E 20-Channel Simultaneous ICP Spectrometer

element	wavelength (nm)	element	wavelength (nm)
aluminum(I)	308.215	scandium(II)	361.384
barium(II)	455.403	silicon(I)	288.158
calcium(II)	317.933	sodium(I)	588.995
chromium(II)	267.716	strontium(II)	421.552
iron(II)	259.940	thorium(II)	401.913
lead(II)	220.353	titanium(II)	337.280
magnesium(I)	383.826	uranium(II)	409.014
manganese(II)	293.930	uranium(II)	424.167
phosphorus(I)	213.618	vanadium(II)	292.402
potassium(I)	769.896	zirconium(II)	343.823

Products ICP-16L generator and torchbox system. The ICP emission is focused onto the entrance slit of a 0.5-m focal length spectrometer (Acton Research Model VM-505) equipped with an intensified photodiode array (EG&G Princeton Applied Research Model 1420) using a 50-mm diameter, 178-mm focal length lens rather than using a fiber optic bundle to couple the ICP emission to the spectrometer as is done in the mobile laboratory. With the spectrometer and diode array used, ICP emission signals for approximately a 10-nm region of the spectrum can be acquired simultaneously. The LA-ICPAES system is calibrated for uranium by ratioing the net intensities of the U(II) 409.014-nm and Si(I) 410.293-nm emission lines for five soil standard samples: a soil blank and soil samples containing 50, 100, 250, and 500 ppm U. Uranium concentrations in the site samples analyzed are determined from the resulting calibration curve.

A CEM Corp. Model MDS-2100 microwave dissolution system is used for digestion of the soil samples. The method used was developed using EPA Method 3051 and CEM Application Note OS-14 as guidelines. A total of 1 g of soil (weighed to the nearest milligram) is transferred to a lined digestion vessel. An acid mixture consisting of nitric, hydrofluoric, and hydrochloric acids and water is added. Reagent-grade acids (Fisher Scientific) are used. The vessel is then sealed, and a two-step microwave digestion program is performed. In step one, low power is used to decompose organics present in the sample; in step two, full power is used for the dissolution of the inorganic matter in the soil. Following the microwave digestion, a saturated solution of boric acid is added to

Table 2. Microwave Dissolution Procedure

sample	1 g of soil (weighed to the nearest milligram into a lined digestion vessel)
acid mixture	8 mL of nitric acid (70%) 6 mL of hydrofluoric acid (48%) 3 mL of hydrochloric acid (37%) 10 mL of water

Microwave Digestion Program

	stage 1	stage 2
power (%)	40	100
pressure (psi)	40	120
time (min)	30	60
time at set pressure (min)	20	45

post-digestion reagent: 30 mL of a saturated solution of boric acid (boric acid in water)

transfer solution from digestion vessel to 100-mL volumetric flask and dilute to volume with water; transfer solution to polyethylene bottle

complex "free" fluoride ions. The resulting solution is transferred to a volumetric flask and brought to volume (100 mL) with water. The details of the microwave digestion procedure used are given in Table 2. A 90-min microwave digestion run is used to effect a "complete" dissolution of the sample rather than the EPA Method 3051 leaching process. Microliter volumes of a 1000 ppm U stock solution (High-Purity Standards, Charleston, SC) are added to aliquots of the microwave dissolution solution to prepare standard addition solutions containing 1, 4, and 10 ppm U. The microwave dissolution solution and standard additions are subsequently analyzed by solution nebulization ICPAES. A CETAC Technologies Model U-5000 ultrasonic nebulizer is used for sample introduction into the ICP. The ICP and spectrometric system used are described in the previous paragraph. The ICP emission signal for the U(II) 409.014-nm line is accumulated (scan averaged) for 1 min using the photodiode array for the four solutions. The U concentration in the dissolved sample is determined by linear regression using the standard addition data.

Results and Discussion

The LA-ICPAES technique was used to determine U concentrations in the soil at 80 sites in the field. The sampling areas were prepared on a 20 × 20 m grid by removing vegetation (the top layer of sod) and rocks from the sites. The response of the LA-ICPAES system was calibrated for U prior to analyzing any of these sites. A soil blank and samples containing 100 and 1000 ppm U were analyzed on the standards sampling station. Emission signals for the U(II) 409.014- and U(II) 424.167-nm emission lines (the peak line intensity minus the intensity at a selected background correction point) were determined using the TJA spectrometer. The intensities for the two U lines were ratioed to the measured Si(I) 288.158-nm and Fe(II) 259.940-nm emission lines to generate calibration curves of intensity ratio versus U concentration. The ICP emission signals were integrated for 30 s at the peak and 30 s at the background correction point during the laser ablation sampling. Three consecutive determinations were made, for a total data acquisition time of 3 min. The two U lines selected were chosen for a number of reasons. The lines are intrinsically intense emission lines, being two of the most sensitive ICPAES lines for U (*15*, *16*). These lines are subject to minimal spectral

Table 3. Technique Comparison for Uranium Concentrations in Field Soil Samples

	microwave dissolution, standard addition determination		field LA-ICPAES		laboratory LA-ICPAES	
name	value (ppm)	95% CI[a]	value (ppm)	95% CI[b]	value (ppm)	95% CI[b]
a1	19.0	8.9	<20		45.7	48.7
a2	21.1	9.8	<20		<20	
a3	43.7	10.0	48	85	37.1	48.9
c1	23.1	6.7	<20		24.2	49.3
c2	28.2	5.4	21	92	22.9	49.4
e9	37.4	8.3	54	83	<20	
k2	72.9	6.5	156	80	34.9	49.0
k3	124.1	10.3	112	85	101.4	47.5
m2	105.8	11.6	285	88	70.6	48.1
q3	102.5	6.1	58	84	74.3	48.0
u1	63.2	13.4	84	93	36.5	48.9
u7	113.1	3.6	224	79	80.7	47.9
w5	62.2	6.0	217	91	29.1	49.2
w11	53.3	7.7	180	83	36.0	49.0
y1	54.6	10.8	112	83	20.9	49.4

[a] Confidence interval for predicted x from a known value of y = 0. [b] Confidence interval for predicted x from a measured value of y = measured intensity.

interference from elements such as Si, Al, and Fe that are present at high concentrations in soil matrices. For this application, fiber optic transmission is also a consideration in line selection. The light-transmitting characteristics of the silica fibers used are the best in the infrared region of the spectrum and decrease gradually throughout the visible and ultraviolet, falling off dramatically for wavelengths less than 250 nm (*17*). For two lines of comparable emission strengths, the longer wavelength transition will be a more sensitive line in fiber optic systems.

After the LA-ICPAES technique was calibrated, the site samples were analyzed. The process involved the following steps. The mobile lab was driven to a position such that up to four different sites could be analyzed by manually positioning the end effector at the site to be sampled. After the mobile lab was in position, the 100 ppm U soil standard was analyzed as a quality control sample. The data for this sample was used to normalize the calibration curves prior to analyzing the site samples. Prior to moving the mobile lab to the next set of sites to be analyzed, the 100 ppm U soil sample was analyzed again. The soil blank sample was analyzed by LA-ICPAES after every 10 site samples to determine if carry-over or memory effects were occurring. No evidence of uranium emission for the soil blank sample was observed throughout the course of the field analysis.

The U concentrations for 15 of the 80 sites analyzed in the field by LA-ICPAES are shown in Table 3. The values are those determined using the U(II) 409.014/Si(I) 288.158 calibration curve. The relative amount of Fe in the soil at the sites analyzed varied by as much as a factor of 2 throughout the site. The amount of Si in the soil was assumed to be constant across the sampling area and equal to that in the calibration standard samples. A spectral interference at the point selected for background correction for the U(II) 424.167-nm line yielded unreliable U concentrations for this line. Therefore, the concentrations reported are those determined from the U(II) 409.014/Si(I) 288.158 intensity ratios. The values are the average of three consecutive determinations for a sample site. The uncertainties in the determined values are also tabulated, at the 95% confidence interval (CI). The uncertainties are large relative to the determined U concentrations for the sites analyzed, with 95% CI values of 80–93 ppm U. The magnitude of the uncertainty is due primarily to the uncertainty in the calibration curve, shown in Figure 2.

The U concentrations determined by laboratory LA-ICPAES analysis of the 15 site samples are presented in Table 3. The values listed are the averages of three consecutive determinations for each sample. Triplicate analyses of the five calibration samples (the soil blank and 50, 100, 250, and 500 ppm U in soil) were also performed to generate the U(II) 409.014/Si(I) 410.293 calibration curve, which is shown in Figure 3. The Si(I) 410.293-nm line was used for the analysis in this case, because it is the only Si line within the spectral window of the U(II) 409.014-nm line on the diode array such that U and Si emission signals can be acquired simultaneously. The LA-ICPAES signals were integrated (scan averaged) using the diode array for 1 min for each determination. The 95% CI uncertainties for the U concentrations determined by laboratory LA-ICPAES are approximately 50 ppm U (see Table 3).

The results for the microwave dissolution and standard addition determination of U by solution nebulization ICPAES for the 15 samples analyzed are also presented in Table 3. The values are the averages of duplicate or triplicate microwave digestions and subsequent standard addition determinations of U. The values listed in Table 3 have been converted from U concentration in solution to concentration (in ppm) for the solid soil samples. An ultrasonic nebulizer was used for sample introduction into the ICP rather than a conventional pneumatic nebulizer because of the improved detection limits attainable using the ultrasonic nebulizer. Detection limits on the order of 0.1 ppm U are typical for pneumatic nebulization (*15, 16*). For ultrasonic nebulization, the detection limit for U is approximately 0.01 ppm (*18*). For the microwave dissolution procedure used, this corresponds to a detection limit for U in soils of approximately 1 ppm (in the solid). The 95% CI uncertainties for the U concentrations determined, shown in Table 3, range from 4 to 13 ppm U. An example standard addition curve with its 95% CI limits is shown in Figure 4 for site sample M2. The intensity of the U(II) 409.014-nm emission line for the microwave digestion solution for M2 (0 ppm U added) and for the 1, 4, and 10 ppm U standard additions to the microwave digestion solution for M2 are plotted. The U concentration for M2 is calculated by linear regression from the standard addition curve.

The confidence intervals in all of these determinations were calculated from the uncertainties in slope and intercept for the linear regression fits to the LA-ICPAES calibration curves or the solution nebulization ICPAES standard addition data. For the calibration curves, the confidence interval was calculated using the following formula:

$$95\%\ \mathrm{CI} = \pm t_{0.05}(\mathrm{df}) b^{-1} [\sigma_y^2 (1/n + 1/m) + (\Delta x)^2 \sigma_b^2]^{1/2} \quad (1)$$

where $t_{0.05}(\mathrm{df})$ is the t distribution for a two-tailed distribution with a 5% probability of a larger value for df (degrees of freedom), b is the fitted slope, σ_y is the standard error in y determined for the fit, n is the number of points in the calibration, m is the number of repetitions determined for the unknown, Δx is the difference in

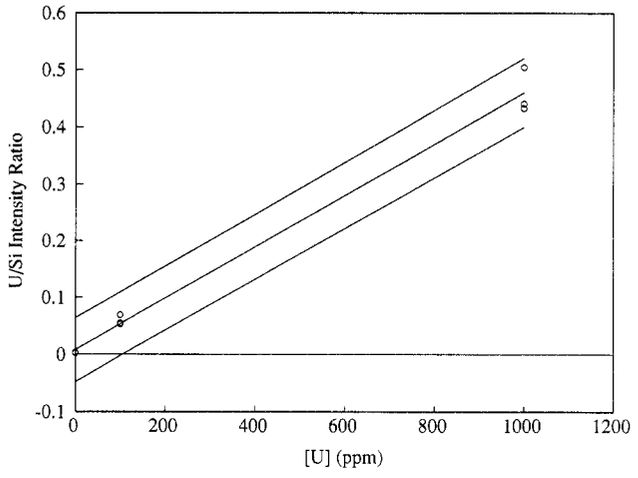

Figure 2. Field LA-ICPAES calibration curve for the U(II) 409.014/Si(I) 288.158 intensity ratio versus U concentration, determined using the TJA ICAP 61E spectrometer. Triplicate analyses of the soil blank and samples containing 100 and 1000 ppm U in soil were performed to generate the calibration curve. The 95% CI limits for the calibration curve are indicated.

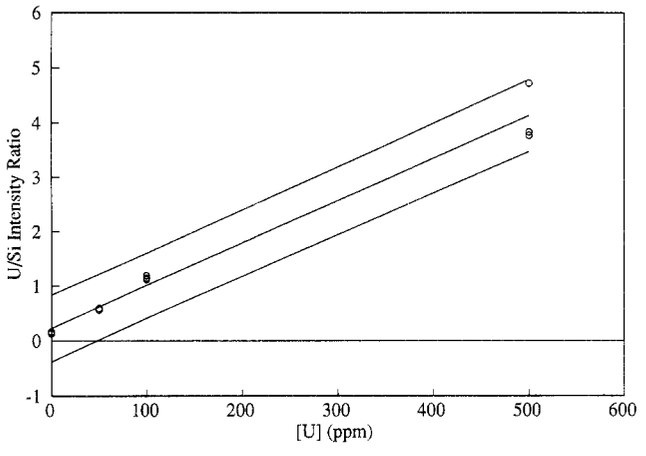

Figure 3. Laboratory LA-ICPAES calibration curve for the U(II) 409.014/Si(I) 410.293 intensity ratio versus U concentration, determined using the photodiode array spectrometer. Triplicate analyses of the soil blank and samples containing 50, 100, and 500 ppm U in soil were performed. The 95% CI limits for the calibration curve are indicated.

concentration between the determined value and the average concentration of the calibration set, and σ_b is the standard error of the slope from the fit (*19*). For the LA-ICPAES determinations in the field, n was 9 and m was 3. The term σ_y^2/m reflects the distribution of y (emission intensity ratios), which may be measured for a given value of x (uranium concentration). For the standard addition method, the value of y at the intercept is extrapolated to a value of zero, so there is no measurement error associated with that value, and the $1/m$ term is not applicable. As a result, all else being equal, standard addition determinations are inherently more precise since they involve the determination of concentration at a known value of intensity (zero) rather than a measured intensity. Examination of the individual terms in this expression for each of the methods shows that the large uncertainties in determinations for the field LA-ICPAES system are predominantly due to the σ_y^2 term despite the number of repetitions for samples and calibration standards. We attribute this large error evident in the calibration curve (Figure 2) to the observed spectrometer drift due to the lack of sufficient environmental controls in the mobile

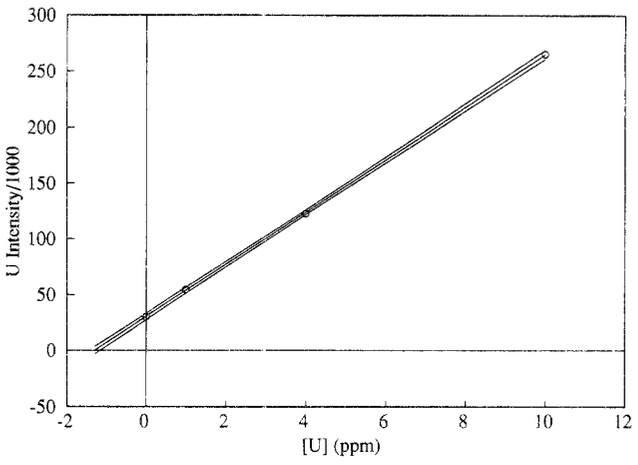

Figure 4. Standard addition curve obtained for microwave dissolution and standard addition determination of U using solution nebulization ICPAES, for site sample M2. The intensity of the U(II) 409.014-nm line is plotted for the solution resulting from microwave digestion (0 ppm U added) and for solutions containing standard additions of 1, 4, and 10 ppm U. The 95% CI for the regression line is indicated.

laboratory and a spectrometer system that was not temperature controlled. Errors for laboratory determinations are therefore noticeably smaller than for the field determinations. Differences between laboratory laser ablation and nebulization of dissolved samples are the subject of ongoing studies in this laboratory. Some possible improvements include using laser power densities higher than those deliverable through fiber optics and using a standard addition method with laser ablation.

The validity of these large calculated confidence intervals for the field analyses may be verified through examination of 57 quality control samples analyzed throughout the field test. The same 100 ppm U standard sample that was used for the initial calibration was analyzed as a quality control periodically throughout the course of the demonstration. The determined values for these tests are plotted in Figure 5 as a histogram on a 10 ppm interval. Also plotted are the 95% CI limits for a 100 ppm sample based on the field LA-ICPAES calibration. It should be noted that of the 57 determinations, 55 or 96% fall within the 95% CI. Tests for skewness and kurtosis show negligible deviation from a normal distribution for this data set. A χ^2 goodness of fit test of a normal distribution fit to the 57 samples gives a <50% probability of a greater value of χ^2, indicating that the fitted normal distribution is a reasonable model for this data. This fit determined a mean value of 115 ppm and a standard error of the distribution of 34 ppm for the 100 ppm sample compared to the standard error for the calibration at 100 ppm of 33 ppm (*19*). The quality control samples were subject to the same experimental fluctuations and errors as the calibration set, and this is reflected in the distribution shown in Figure 5.

A number of facts are evident from the data presented in Table 3 and Figures 2–4. The uncertainty in the LA-ICPAES field-determined U concentrations is larger than that for the laboratory-determined LA-ICPAES values, which, in turn, is larger than that for the microwave digestion and standard addition determination for U. This is not unexpected; field analytical determinations are generally less reliable than laboratory-determined values due to poorer control of environmental factors. For 11 of the 15 site samples analyzed, the U concentrations

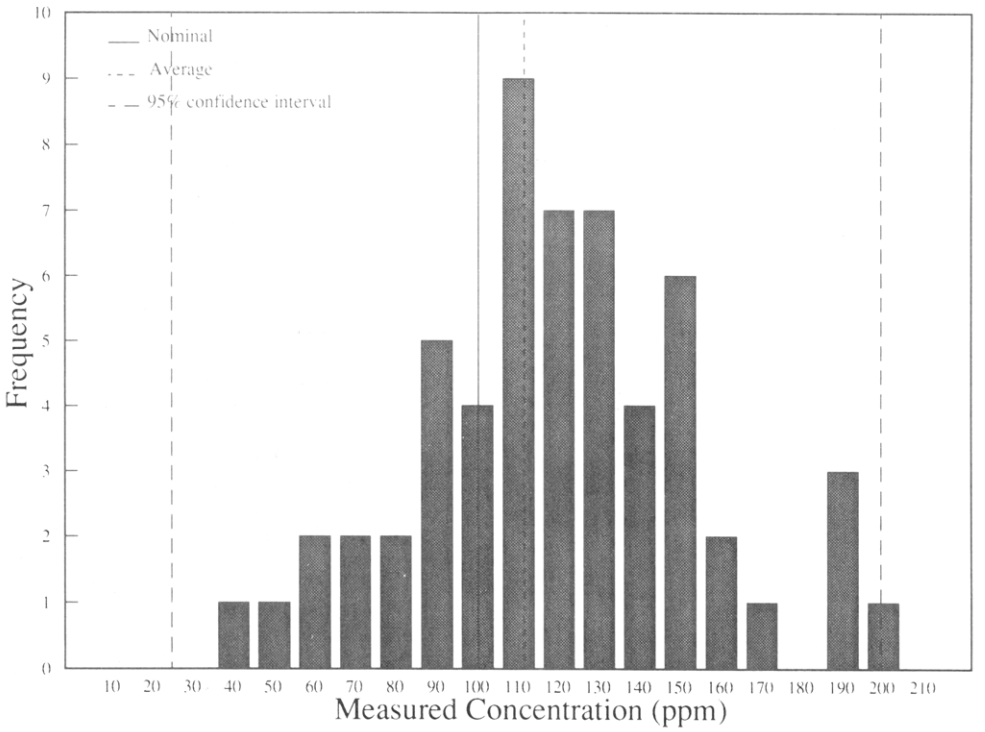

Figure 5. Histogram of concentrations determined in the field using LA-ICPAES for 57 quality assurance checks of a soil sample spiked with 100 ppm uranium. Also shown are the nominal value (100 ppm), the average value of the determinations (115 ppm), and the 95% CI for the normal distribution fitted to this data (±89 ppm).

determined in the field by LA-ICPAES agree with the values determined in the lab, within the uncertainty of the determined concentrations. The four that do not agree are sites M2, U7, W5, and W11. The U concentrations determined by LA-ICPAES in the field are typically higher than the values determined in the lab, by a factor of 2–3 for some of the samples. These differences may be attributed, at least in part, to the difference between in situ sampling of an unprepared surface and analysis of a sample collected over some depth, which is large compared to the depth sampled by the laser (several microns) and which was dried, ground, and homogenized. The uranium contamination at this site was a surface deposition. Analysis of core samples using the field LA-ICPAES system showed no significant penetration of uranium to a 1-ft depth, indicating a sharp drop in concentration with depth. It should not be surprising then that a depth-averaged homogenized sample shows significantly less contamination than the surface. Other variations may be attributed to heterogeneity in the horizontal plane. It is important to note that for the two laboratory methods of analysis used, the U concentrations determined for the 15 site samples agree, within the uncertainty of the determined values. This is evidence that the differences between field and lab results are not a result of laser ablation variations compared to standard liquid introduction techniques but are really differences between the concentrations in the sampled materials.

Conclusions

The agreement between the field- and laboratory-determined U concentrations is promising, especially considering the fact that this was the first operation of the mobile laboratory LA-ICPAES system in a field test. The uncertainties in the U concentrations determined by LA-ICPAES in the field are large, so the results can vary by a relatively large amount yet still be in agreement, within the uncertainty of the determined values. Some of the uncertainty in the U concentrations determined by LA-ICPAES in the field can be attributed to operational conditions in the mobile lab. For instance, the temperature and humidity in the mobile lab varied more than the specified operation limits for some of the instrumentation, including the TJA spectrometer. Temperature and humidity fluctuations cause misalignment of the spectrometer and lead to analytical errors. Therefore, a number of improvements to the mobile lab are expected to improve the quality of the analytical data obtained in the field. Some of the uncertainty in the LA-ICPAES determinations in the field and laboratory is due to the uncertainty in the calibration (Figures 2 and 3). The use of U/Si intensity ratio calibration curves for quantitation appears to limit the precision of the LA-ICPAES technique, which is particularly significant for samples with concentrations in the low end of the range of the calibration. Development of an absolute quantitation method to account for variations in laser ablation efficiency due to changes in laser power and focus at the sample, differences in material transport out of the ablation cell and into the ICP, and for samples of differing soil composition, moisture content, and compaction may be required to significantly improve the precision of the LA-ICPAES technique. Differences in the results for the laboratory and field results may be largely attributed to the differences between surface sampling and analysis of depth-averaged homogenized samples.

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